

Supplemental material associated with the paper entitled

“Lattice strain in irradiated materials unveils a prevalent defect evolution mechanism”

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Materials and methods

Characteristics of the studied materials

c-ZrO₂, MgO and ZrC were {100}-oriented, commercial single-crystals. c-ZrO₂ samples (stabilized with 9.5 mol % Y₂O₃) and MgO samples were synthesized by Crystal GmbH. ZrC crystals were provided by MaTeck GmbH. The UO₂ (0.3% ²³⁵U) samples were {111}-oriented UO₂ single-crystals produced at the Joint Research Center in Ispra (Italy).

These four materials exhibit different characteristics. In terms of crystalline structure, UO₂ and c-ZrO₂ share the fluorite structure, but there are native vacancies in c-ZrO₂ due to the incorporation of Y₂O₃ to stabilize the cubic structure at room-temperature (RT); MgO and ZrC have a rock-salt structure. The bonding in the three oxides has a pronounced ionic character whereas it has a marked metallic character in ZrC. Defect energetics are different in the four materials, notably the relative (interstitial and vacancy) defect migration energies of the elements of the two sub-lattices, but in all materials at least one interstitial defect species is highly mobile¹⁻⁴.

Ion irradiations

UO₂ and MgO samples were irradiated at the SCALP facility (CSNSM, Univ Paris-Sud and CNRS, Université Paris-Saclay, France)⁵; irradiations of UO₂ were performed at room-temperature (RT) with 20 keV He⁺ ions and 500 keV Ce³⁺ ions and MgO irradiations were carried out at 573 K with 1.2 MeV Au⁺ ions. ZrC samples were irradiated at RT with 1.2 MeV Au⁺ ions at both JANNuS-Orsay (CSNSM) and JANNuS-Saclay (CEA/DEN/SRMP)⁶ platforms. c-ZrO₂ samples were irradiated at 80 K with 4 MeV Au²⁺ ions with the 3 MeV Tandetron of the Instituto de Fisica of the Universidade Federal of Rio Grande do Sul. Different ion-fluence ranges were used for the four materials in order to catch the whole strain development process for each material. In all cases, it was taken care to tilt the sample holder by 7° with respect to the ion beam direction to prevent any channelling effect of the bombarding ions in the crystals. A beam raster system was used to ensure a homogeneous irradiation over the samples' surface. The ion flux was kept below 5 x 10¹¹ cm⁻².s⁻¹ to avoid any sample overheating. Detailed irradiation conditions are given in^{7, 8, 9} and⁴ for c-ZrO₂, UO₂, MgO and ZrC samples, respectively.

XRD measurements and simulations

c-ZrO₂, MgO and ZrC crystals were characterized by XRD with the diffractometer of the CTU-Minerve of IEF (Orsay, France). XRD measurements of the UO₂ samples were conducted at ISC (Rennes, France). A complete description of these two apparatus is given in⁷ and⁸ for the former and the latter, respectively. Note that in both cases an intense, monochromatic (Cu-K_{α1}) and weakly divergent (~18 arcsec) X-ray beam was used. This beam was delivered by a very similar primary optics system based on a parabolic multilayer mirror and a four-reflection Ge(220) monochromator. A three-reflection Ge monochromator coupled with a point detector was used for the IEF diffractometer, whereas a 1D position sensitive detector was used at ISC. Symmetric $\theta/2\theta$ scans were recorded around the (400) reflection of c-ZrO₂, MgO and ZrC and around the (222) reflection of UO₂ over an angular range wide enough to include all the diffraction signal coming from the irradiated

region of the crystals. The strain depth profiles were retrieved from the simulation of these scans using the RaDMaX program¹⁰, where the difference in instrumental resolution of the diffractometers was specifically taken into account.

Computational work

The Molecular Dynamics simulations of Frenkel Pair Accumulation (MD-FPA) methodology gives access to the response of materials to irradiation as a function of irradiation level¹¹. It is designed to mimic ballistic (so-called nuclear) damage in materials circumventing displacement cascades as long as they produce point defects only, which is the case for the materials studied in this work. This methodology consists in creating Frenkel pairs (here uranium interstitial – vacancy pairs) at chosen time intervals, in the framework of MD simulations. Calculations were performed (at 300 K) using a modified version of the LAMMPS code¹². Details can be found in¹³ and references therein.

Rate Equation Cluster Dynamics calculations deal with the evolution of the concentration of a population of defect clusters (formed by either vacancies or interstitials) through chemical rate equations. These equations describe the creation of single defects by irradiation, and the growth or shrinkage of clusters through the emission or absorption of mobile species, which are restricted to single defects in the present case. A complete description of the CRESCENDO code can be found in^{14,15}, and details of the method applied for ZrC are given in⁴.

Experimental XRD data

Figure 1 shows a few representative experimental X-ray diffraction (XRD) curves obtained on the four different studied systems; ion fluences are expressed in displacement per atoms (dpa). Part of these data was already published (see [8] for UO₂, [7] for c-ZrO₂, [16] for MgO and [4] for ZrC).

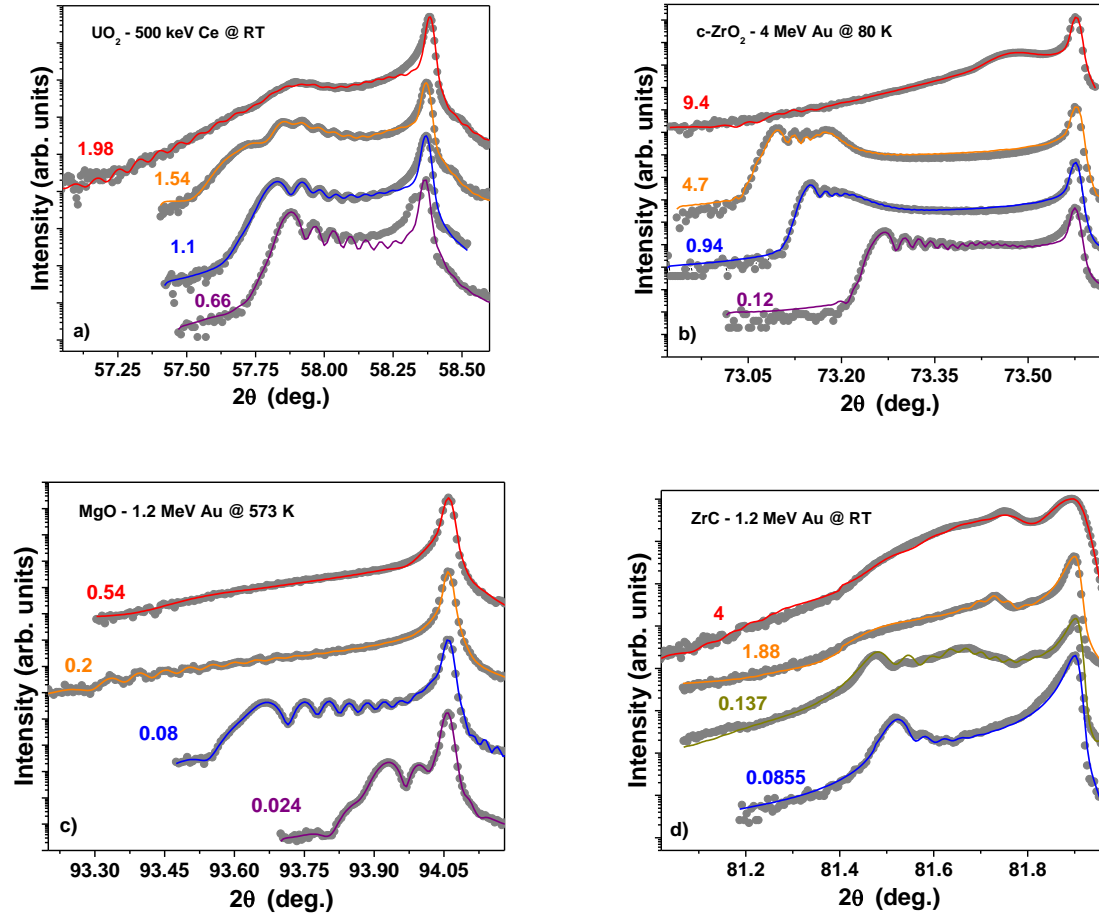


Fig. 1: XRD experimental data (grey dots) obtained in symmetric (so-called θ - 2θ) configuration on four different materials at different ion fluences expressed in dpa. Solid lines are simulations obtained with the RaDMaX program¹⁰.

All curves exhibit an intense peak on the high-angle side that corresponds to the diffraction by the pristine region of the bulk crystals beneath the irradiated layer. The additional signal on the low-angle side comes from the damaged part of the samples. More details on the exact origin and shape of these curves can be found in^{17,18}. These XRD curves were simulated with the dedicated RaDMaX program¹⁰ to retrieve the strain depth-profiles; simulations are displayed as solid lines. It is worth mentioning that, notably at high dpa, simulations may differ from previously published ones owing to the new information provided by our recent computational work presented in the main paper. A very good agreement between simulations and experimental data is observed, strongly suggesting that the strain profiles are accurate and relevant.

On the agreement between experiments and calculations

In the present work, we implemented an approach based on the use of an experimental characterization technique, namely XRD, combined with two computational methods, namely molecular dynamics (MD) and rate equation cluster dynamics (RECD), to determine and interpret the strain variation processes in irradiated materials. The computational work was carried out to provide data not accessible experimentally for a better understanding of the origin of the strain variations. We obtained an overall good agreement between experimental and computational data. There are yet some differences that, although they do not question in any case the main results presented in this work, should be addressed here.

Regarding the Frenkel Pair Accumulation (MD-FPA) calculations, the higher strain values determined by simulations (as compared to experimental values) are due to an overestimation of the point defect concentration owing to a high defect creation rate. Similarly, this high creation rate implies that all defects do not have enough time to be trapped by the dislocation loops/lines, which explains why the strain relaxation is not total, contrary to what happens in the material during an actual experiment. To finish, the difference in dpU value at which relaxation occurs (which exists even for the two different - He and Ce - experiments), most likely comes from a misevaluation of the number of surviving uranium Frenkel pairs by the SRIM code (see ^{19,20}).

For the RECD calculations, a difference arises in the depth scale between calculated and experimentally-determined strain depth-profiles, which can be essentially explained by the fact that the diffusion of interstitial clusters is neglected, so that only mono-interstitials diffuse beyond the primary damage region, thus decreasing the spread of the damage deeper in the material. There is also a difference in the dpa level at which the strain relaxation takes place that can be ascribed to the assumptions used for the defect source term in RECD calculations, in particular the rate of surviving defects inside a collision cascade⁴. The slight difference in the strain magnitude is likely due to both the defect source term and to the underestimation of the relaxation volume of small dislocation loops owing to second order elasticity theory effects²¹.

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